

PATENT SPECIFICATION

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(54) FIXING OF HEAVY METAL OR HEAVY METALLIC COMPOUND

(71) We, NIPPON SODA COMPANY LIMITED, of No. 2-1, Ohtemachi 2-chome, Chiyoda-ku, Tokyo, Japan, a company organised under the laws of Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to fixing of heavy metal or heavy metallic compound and more particularly to treatment of a slurry or solution, or soil, containing heavy metal or heavy metallic compound to fix the metal or metallic compounds and thereby prevent same from dissolving in liquid, and to a construction cement having an agent to fix heavy metal or heavy metallic compounds.

In recent times the environment has been subject to pollution by heavy metals or heavy metallic compounds discharged from mines, factories, cars, hospitals, laboratories or derived from waste products such as electric batteries and lamps. These heavy metals or heavy metallic compounds dissolve in river or subterranean water, and may be absorbed by plants and animals and in turn by human beings.

According to a first aspect of the present invention, there is provided a method of treating a slurry or solution containing heavy metal or heavy metallic compound to fix the metal or metallic compound, comprising the step of mixing with the solution or slurry 0.1 to 50.0—by weight of an aliphatic dithiocarbamate compound, wherein the aliphatic dithiocarbamate compound is a compound having an aliphatic chain, which may contain a nitrogen atom in place of a carbon atom, and at least two dithiocarbamic acid groups



or alkali metal, alkaline earth metal or ammonium hydroxide salts or esters thereof. The aliphatic dithiocarbamate compound may be present in a cement composition in an amount of 0.001 to 10% by weight of the composition, the composition being mixed in the slurry or solution in an amount of 20 to 80% by weight.

According to a second aspect of the present invention, there is provided a method of treating soil containing heavy metal or metallic compound, to prevent plants from absorbing the metal or metallic compound, comprising the step of mixing in the soil 0.001 to 10% by weight of an aliphatic dithiocarbamate compound, wherein the aliphatic dithiocarbamate compound is a compound having an aliphatic chain, which may contain a nitrogen atom in place of a carbon atom, and at least two dithiocarbamic acid groups



or alkali metal, alkaline earth metal or ammonium hydroxide salts or esters thereof. Preferably, 0.01 to 2.0% by weight of the compound is mixed with the soil.

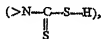
According to a third aspect of the present invention, there is provided a construction cement having a heavy metal or heavy metallic compound fixing agent, the agent being present in an amount of 0.001 to 10% by weight and comprising a compound prepared by reacting an amine selected from ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, propylenediamine, dipropylenetriamine, tripropylene tetramine, tetrapropylene pentamine and pentapropylenehexamine with carbon bisulfide, one gram molecule of amine to 2 to 6 gram molecules of carbon bisulfide being employed.

In the methods and construction cement provided by the invention, an aliphatic dithiocarbamate compound is used as a fixing agent for heavy metals or heavy metallic compounds by being mixed with soil, water or slurry wastage containing heavy metal or heavy metallic compound. The fixing agent reacts with the heavy metal or heavy metallic compound to form a compound insoluble in water.

This fixing agent can have less conventional usages, for example, when slurry or granular wastage containing heavy metals or heavy metallic compounds, such as mud containing a mercuric compound byproduct of an electrolysis plant, is packed in a concrete container and dumped in the sea or buried in the ground, heavy metals or heavy metallic compounds may be dissolved by water and exude through the wall of the container, which results in pollution of the environment. In this case, mixing of the agent in the mud in an amount of 0.1 to 50% by weight may prevent the exudation of the heavy metal and heavy metallic compounds. Further, if the agent is homogeneously mixed in concrete or mortar in an amount of 0.001% to 10%, preferably 0.001 to 1% by weight, of the cement used in the concrete or mortar, the agent may prevent heavy metals and heavy metallic compounds from passing through the concrete or mortar. Moreover, setting material, which solidifies to be tough, for example, cement such as Portland cement or the raw material of a resin, and which contains 0.001% to 10%, preferably 0.001% to 1%, by weight of the agent, can be used for packing harmful heavy metallic compounds, and walls or other constructions, such as drainage pipes, made from such material may resist the passage therethrough of heavy metals and heavy metallic compounds.

The agent may be used in agriculture, as when a soil contains a heavy metal or heavy metallic compound, crops planted in the soil may absorb the heavy metal or heavy metallic compound. In this case, the absorption of the heavy metal or heavy metallic compound by the crops may be prevented by adding the agent to the soil. Conveniently, 0.001 to 10%, preferably 0.01 to 2%, by weight of the agent is added and homogeneously mixed in the soil. The agent is effective, particularly when the soil has weak acidity of alkalinity of pH 5 to 11, against mercury, copper and cadmium. Moreover, heavy metal or heavy metallic compound in irrigation water may be precipitated by adding the agent to the water.

In the present invention, aliphatic dithiocarbamate compound means a compound having an aliphatic chain which may contain a nitrogen atom in place of a carbon atom and at least two dithiocarbamic acid groups



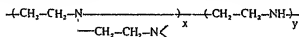
which is contained in the compound in the form of acids ($R-NHCSSH$ or

$R-NHSSH$) or salts or esters of alkali metals, alkaline earth metals and ammonium hydroxide of the dithiocarbamic acid groups.

The following are examples of aliphatic dithiocarbamate compounds that may be used:

ethylene-di-thiocarbamic acid ($HS_2CNHCH_2CH_2NHCS_2H$)
 N,N,N-tris(dithiocarboxyl)ethylenediamine
 N,N,N',N'-tetra(dithiocarboxyl)ethylenediamine
 1,3- or 1,2-propylenebis(dithiocarbamic acid)
 N,N,N'-tris(dithiocarboxyl)propylenediamine
 N,N,N',N'-tetra(dithiocarboxyl)propylenediamine
 tetramethylenebis(dithiocarbamic acid)
 tris or tetra-(dithiocarboxyl)propylenediamine
 hexamethylenebis(dithiocarbamic acid)
 octamethylenebis(dithiocarbamic acid)

	N,N^3 -bis(dithiocarbonyl)diethylenetriamine ($HS_2CHNCH_2CH_2NHCH_2CH_2NHCS_2H$)	
	N^1,N^2,N^3 -tris(dithiocarbonyl)diethylenetriamine N^1,N^1,N^2,N^2 -tetra(dithiocarbonyl)diethylenetriamine	
5	N^1,N^1,N^2,N^2,N^3 -penta(dithiocarbonyl)diethylenetriamine N^1,N^1,N^2 (dithiocarbonyl)triethylenetetramine ($HS_2CNHC_2H_4NHC_2H_4NHC_2H_4NHCS_2H$)	5
	N^1,N^2,N^1 -tris(dithiocarbonyl)triethylenetetramine N^1,N^2,N^2,N^3 -tetra(dithiocarbonyl)triethylenetetramine	
10	N^1,N^1,N^2,N^2,N^3,N^3 -penta(dithiocarbonyl)triethylenetetramine $N^1,N^1,N^2,N^2,N^3,N^3,N^4$ -hexa(dithiocarbonyl)triethylenetetramine N^1,N^2 -bis(dithiocarbonyl)tetraethylenepentamine ($HS_2SNHC_2H_4NHC_2H_4NHCS_2HC_2H_4NHC_2H_4NHCS_2H$)	10
	N^1,N^2,N^2,N^3 -tris(dithiocarbonyl)tetraethylenepentamine N^1,N^2,N^2,N^3,N^4 -tetra(dithiocarbonyl)tetraethylenepentamine	
15	N^1,N^2,N^2,N^3,N^4 -penta(dithiocarbonyl)tetraethylenepentamine $N^1,N^1,N^2,N^2,N^3,N^3,N^4$ -hepta(dithiocarbonyl)tetraethylenepentamine N^1,N^2,N^2,N^3,N^4,N^4 -hexa(dithiocarbonyl)tetraethylenepentamine N^2,N^2 -bis(dithiocarbonyl)pentaethylenhexamine	15
	N^1,N^2,N^1 -tri(dithiocarbonyl)pentaethylenhexamine N^1,N^2,N^1,N^2 -tetra(dithiocarbonyl)pentaethylenhexamine	
20	N^2,N^2,N^2,N^3,N^4,N^4 -hexa(dithiocarbonyl)pentaethylenhexamine bis(dithiocarbonyl)propylenediamine tris(dithiocarbonyl)dipropylenetriamine	20
	N^1,N^4 -bis(dithiocarbonyl)tripropylenetetramine N^1,N^2,N^4 -tris(dithiocarbonyl)tripropylenetetramine	
25	N^1,N^2,N^2,N^4 -tetra(dithiocarbonyl)tripropylenetetramine N^2,N^1,N^2,N^2,N^3,N^4 -penta(dithiocarbonyl)tripropylenetetramine N^2,N^2,N^2,N^2,N^3,N^4 -hexa(dithiocarbonyl)tripropylenetetramine	25
	N^2,N^3 -bis(dithiocarbonyl)tetrapropylene-pentamine N^2,N^2,N^4 -tris(dithiocarbonyl)tetrapropylene-pentamine	
30	N^2,N^2,N^2,N^3 -tetra(dithiocarbonyl)tetrapropylene-pentamine N^2,N^2,N^2,N^3,N^4 -penta(dithiocarbonyl)tetrapropylene-pentamine N^2,N^1,N^2,N^2,N^3,N^4 -hexa(dithiocarbonyl)tetrapropylene-pentamine	30
	N^2,N^2 -bis(dithiocarbonyl)dibutylenetriamine N^1,N^2,N^3 -tris(dithiocarbonyl)dibutylenetriamine	
35	N^1,N^2,N^3 -tris(dithiocarbonyl)tributylenetriamine N^1,N^2 -bis(dithiocarbonyl)tributylenepentamine N^1,N^2,N^3 -tris(dithiocarbonyl)tetrabutylene-pentamine	35
	N^2,N^2,N^2,N^3,N^4 -penta(dithiocarbonyl)tetrabutylene-pentamine N^2,N^1,N^2,N^2,N^3,N^4 -hexa(dithiocarbonyl)tetrabutylene-pentamine	
40	N^2,N^2 -bis(dithiocarbonyl)diethylenetriamine N^1,N^2,N^3 -tris(dithiocarbonyl)tributylenepentamine N^1,N^2,N^3 -tris(dithiocarbonyl)tetrabutylene-pentamine N^1,N^2,N^3,N^4 -tetra(dithiocarbonyl)tetrabutylene-pentamine poly(N -dithiocarbonyl)polyethylenimine (polyethylenimine have the following structure:	40



45	and alkali metal (e.g. Na and K), alkaline earth metal (e.g. Be, Mg, Ca and Ba) or ammonium hydroxide salts of above said acids, and the esters with the alcohols having 1 to 4 carbon atoms.	45
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	An aliphatic dithiocarbamate compound having less than 4 carbon atoms shows phytotoxicity, so aliphatic dithiocarbamate compounds having 5 or more carbon atoms are preferred.	
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50	These dithiocarbamate compounds can be easily prepared from corresponding amine compounds such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenhexamine, dipropylenetriamine, tripropylene-tetramine, tetrapropylene-pentamine, dibutylenetriamine, tributylene-triamine and tetra-butylene-pentamine by reacting with carbon bisulfide in the presence of a solvent	50
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55	such as acetone, methyl ethyl ketone and water and alkaline catalysts such as sodium hydroxide, potassium hydroxide and ammonium hydroxide, at a temperature of from -10°C to 60°C, preferably 20°C to 45°C. The reaction mixture contains dithio-carbamate compound, which has a red-orange or brown colour, in the form of a salt.	55
60	The reaction between the hydrogen atom which combines with the nitrogen atom of amino or imino group and carbon bisulfide proceeds quantitatively. Accordingly, the	60

same number of gram molecules of carbon bisulfide as the proposed number of dithiocarbamate groups of the proposed compound is employed in its preparation.

For example, when two dithiocarbamate groups are intended to introduce in amine compound, two gram molecules of carbon bisulfide are reacted with one gram molecule of amine compound. Ordinarily, aliphatic dithiocarbamate compound can be used as a fixing agent in the form of an aqueous solution, or a carrier can be impregnated with the aqueous solution of aliphatic dithiocarbamate to provide a granular or paste fixing agent. In the latter case, 1 to 30% of the aliphatic dithiocarbamate compound is preferably contained in the carrier.

Many kinds of materials having a porous structure and large specific surfaces can be employed as the carrier, preferably porous material having a large specific surface of more than $1\text{ m}^2/\text{g}$ measured by argon gas adsorption method by use of the BET equation, for example, diatomaceous earth, pumice stone, zeolite, kaolin, vermiculite, alumina (aluminium oxide), silicagel, coke, activated charcoal, graphite, bentonite and foamed urethane resin having open cells.

The fixing agent can selectively react with heavy metal and heavy metallic compounds such as nickel, chromium, zinc, lead, copper, cadmium, silver, arsenic, manganese, bismuth, vanadium and mercury, particularly mercury and compounds thereof, even if these heavy metals or metallic compounds exist as non-ionic or ionic compounds. So far as concerns mercuric and silver compounds, various types of compound can be fixed, for example, metallic oxides such as HgO and Ag_2O , metallic chlorides such as HgCl_2 and AgCl , metallic sulphates such as HgSO_4 , Hg_2SO_4 and Ag_2SO_4 , metallic nitrates such as $\text{Hg}(\text{NO}_3)_2$ and $\text{Hg}_2(\text{NO}_3)_2$, metallic sulphides such as HgS and Hg_2S , and organometallic compounds such as methylmercuric chloride, ethylmercuric chloride, phenylmercuric acetate, ethylmercuric iodide, methylmercuric iodide, ethylmercuric bromide, methylmercuric bromide, phenylmercuric chloride, diphenylmercury and phenylmercuric benzoate are fixed.

Furthermore, cadmium and cadmium compounds can be fixed by the agent, even if the cadmium compounds are non-ionic or ionic, for example, CdSO_4 , CdCl_2 , CdS , CdO and $\text{Cd}(\text{OH})_2$.

Embodiments of the method and of the cement composition according to the present invention, and preparation of fixing agents employed in such embodiments, are illustrated by the following examples. All quantities referred to in the description and appended claims as "parts" or "percent" are "parts by weight" or "percent by weight" respectively unless expressly stated otherwise.

Example 1.

Preparation of fixing agents.

80 parts of NaOH , 500 parts of water and 60 parts of ethylene diamine were mixed together, and 152 parts of carbon bisulfide were added dropwise at 30°C to 40°C under vigorous stirring. After 1 hour of the reaction, nitrogen gas was blown through the reaction mixture to remove any unreacted carbon bisulfide. A brown-orange transparent aqueous solution containing 31.0% of sodium ethylenedithiocarbamate ($\text{Na}_2\text{S}_2\text{CNH}-\text{CH}_2\text{CH}_2\text{NHC(S)Na}$) was obtained. The reaction solution itself was used as a fixing agent.

Examples 2 to 25.

Various kinds of amines, basic compounds and carbon bisulfide, as shown in Table 1, were reacted according to the procedure of example 1 and various kinds of fixing agents were obtained, the fixing agents and raw materials being listed in Table 1.

Example 26.

Aliphatic dithiocarboxyl compounds, identified by the numbers given in Table 1, Portland cement, water and mud containing mercuric compound byproduct from a sodium chloride electrolysis plant were mixed in the proportions given in Table 2 and allowed to solidify into blocks 16 cm high \times 4 cm wide \times 4 cm long. The blocks were allowed to stand for 14 days and then were soaked in quantities of pure water and sea water 4 times the volume of the blocks.

The concentration of mercury in the sea water or pure water was measured after periods of 1 hour, 1 day, 14 days, 1 month and 1 year. The results are listed in Table 2.

The mud originally contained NaCl , $\text{Mg}(\text{OH})_2$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, CaCO_3 , C, about 120 ppm of mercury and about 45% water.

TABLE 1

examp. No.	raw materials (parts)					reaction product of fixing agent		
	amine	alkali	water	CS ₂	temp (°C)	color	aliphatic dithio carbamate compound (%)	note
1	ethylenediamine	60 NaOH	80	500	152	30 40	brown S orange	sodium ethylenebisdithio carbamate (31) needle crystal
2	ethylenediamine	60 Ca(OH) ₂	74	500	152	30 45	orange	Calcium ethylenebisdithio carbamate (31) needle crystal
3	diethylenetriamine	103 NaOH	120	500	228	30 40	brown S orange	tris(dithiocarboxyl sodium) diethylenetriamine (37) —
4	diethylenetriamine	103 Ca(OH) ₂	74	500	228	20 43	pale yellow S green	tris(dithiocarboxyl calcium) diethylenetriamine (36) —
5	triethylenetetramine	146 NaOH	160	800	304	27 40	brown S orange	tetra(dithiocarboxyl sodium) triethylenetetramine (36) —
6	triethylenetetramine	146 Ca(OH) ₂	74	700	304	25 45	pale yellow	tetra(dithiocarboxyl calcium) triethylenetetramine (28) —
7	tetraethylenepentamine	189 NaOH	200	1200	380	15 40	orange	penta(dithiocarboxyl sodium) tetraethylenepentamine (34) —
8	polyethylenimine (m.w. = 1,000)	30 NaOH	32	300	60	28 43	orange	poly n-dithiocarboxyl sodium polyethylenimine (21) —
9	triethylenetetramine	146 NaOH	160	800	228	30 40	orange	tetra(dithiocarboxyl sodium) triethylenetetramine (35) reaction product of example 5 was treated with acid

TABLE I (Continued)

examp. No.	raw materials (parts)					reaction product of fixing agent			
	amine	alkali	water	CS ₂	temp (°C)	color	aliphatic dithio carbonate compound (%)	note	
10	polyethylene amine	30 NaOH	32	1200	380	15 40	orange	poly n-dithiocarboxyl polyethyleneamine (20)	reaction product of example 8 was treated with acid
11	ethylene-diamine	60 NaOH	80	500	152	30 40	pale orange	zinc ethylenedisithio carbonate (28)	reaction product of oample 1 was treated with ZnCl ₂
12	diethylene-tetramine	103 NaOH	160	500	342	20 43	pale red	mixture of tetra and tri-(dithiocarboxyl sodium) diethylene-tetramine (33)	
13	ethylene-diamine	60 NaOH	160	800	304	30 45	orange	N,N,N',N'-tetra(dithiocarboxyl sodium) ethylenediamine	needle crystal
14	triethylene-tetramine	146 NaOH	240	1000	456	30 45	yellow orange	N',N',N',N'-hexa(dithio-carboxyl sodium) triethylene tetramine	needle crystal
15	tetraethylene-pentamine	189 NaOH	280	1200	532	30 45	orange	N',N',N',N',N'-hepta(dithio-carboxyl sodium) tetrapen-tamine	needle crystal
16	1,3-diamino-propane	74 NaOH	80	520	152	30 45	orange	N,N'-di(dithiocarboxyl sodium) diaminopropane	
17	hexamethylene diamine	116 NaOH	80	600	152	30 45	orange	N,N'-di(dithiocarboxyl sodium) hexamethylenediamine	block crystal
18	Octamethylene diamine	144 NaOH	80	700	152	30 45	orange	N,N'-di(dithiocarboxyl sodium) octamethylenediamine	block crystal

TABLE I (Continued)

examp. No.	raw materials (parts)					color	reaction product of fixing agent	
	amine	alkali	water	CS ₂	temp (°C)		aliphatic dithio carbamate compound (%)	note
19	1,3-diamine-propane	74 NaOH	160	700	30 45	orange	N,N,N',N'-tetra(dithiocarboxyl sodium)1,3-diaminopropane	black crystal
20	hexamethylene-diamine	116 NaOH	160	800	30 45	orange	N,N,N',N'-tetra(dithiocarboxyl sodium)hexamethylenediamine	black crystal
21	diethylenetriamine	103 Ca(OH) ₂	74	500	152	orange	N,N'-bis(dithiocarboxyl calcium)diethylenetriamine	
22	triethylenetetramine	146 Ca(OH) ₂	74	500	152	orange	N,N'-bis(dithiocarboxyl calcium)triethylenetetramine	
23	diethylenetriamine	103 NaOH	80	500	152	orange	N,N'-bis(dithiocarboxyl calcium)diethylenetriamine	
24	tetraethylenepentamine	189 NaOH	200	500	380	orange	N,N'-bis(dithiocarboxyl sodium)tetraethylenepentamine	
25	triethylenetetramine	146 NaOH	80	500	152	orange	N,N'-bis(dithiocarboxyl sodium)triethylenetetramine	

TABLE 2

water (parts)	mud (parts)**	cement (parts)	fixing agent (parts) No.s of Table 1	lig concentration (ppm)							
				1 hour		1 day		14 days		1 month	
				not detected*	not detected*	not detected	not detected	not detected	not detected	not detected	not detected
1	2	2	No. 5 (0.001)	sea water	sea water	sea water	sea water	sea water	sea water	sea water	sea water
1	2	2	No. 3 (0.01)	water	water	water	water	water	water	water	water
1	2	2	No. 7 (0.005)	sea water	sea water	sea water	sea water	sea water	sea water	sea water	sea water
1	2	2	No. 10 (0.01)	water	water	water	water	water	water	water	water
1	2	2	No. 11 (0.02)	sea water	sea water	sea water	sea water	sea water	sea water	sea water	sea water
1	2	2	No. 13 (0.03)	water	water	water	water	water	water	water	water
1	2	2	No. 15 (0.005)	sea water	sea water	sea water	sea water	sea water	sea water	sea water	sea water
1	2	2	No. 17 (0.01)	water	water	water	water	water	water	water	water

TABLE 2 (Continued)

water (parts)	mud (parts)**	cement (parts)	fixing agent (parts) No.s of Table 1	test water	Hg concentration (ppm)				
					1 hour	1 day	14 days	1 month	1 year
1	2	2	No. 18 (0.01)	water	not	not	not	not	not
				sea water	detected*	detected	detected	detected	detected
1	2	2	No. 19 (0.01)	water	"	"	"	"	"
				sea water	"	"	"	"	"
1 (control)	2	2	none	water	0.009	0.015	0.042	0.068	0.21
			none	sea water	0.005	0.007	0.016	0.022	0.15

* less than 0.001 ppm

** day weight

Example 27.

500 parts of dry sludge containing copper and copper compound byproducts from a copper electro plating factory and 0.5 part of tetra (dithio carboxyl sodium) tri-ethyleneamine (No. 5 in Table 5) were mixed together and 25 parts of epoxide resin and 25 parts of curing agent (amines) were admixed with the mixture.

The resulting mixture was cured in moulds to produce test blocks each of 4cm X 4cm X 4cm.

The test blocks were soaked in quantities of sea water and pure water 4 times the volume of the blocks. At periods of 1 day, 1 month and 3 months, the copper concentration in the sea water or pure water was measured, and the results are listed in Table 3.

5

10

TABLE 3

composition (parts)		copper sludge	test water	copper concentration (ppm)		
resin	fixing agent			1 day	1 month	3 months
50	tetra(dithiocarbonyl)- sulfamethylene tetraamine (0.5)	500	water	not detected *	not detected	not detected
			sea water	"	"	"
50 (control)	none	500	water	"	0.23	1.5
			sea water	"	0.46	2.4

* less than 0.1 ppm

Example 28.

100 parts of mud, which contained 25ppm of mercury and 38% of water and which was a byproduct of a sodium chloride electrolysis plant, were mixed for 10 minutes with each of several fixing agents, identified by the numbers given in Table 1, to produce slurry.

At periods of 1 hour, 1 week, 1 month, 3 months, 6 months and 1 year, 8gms of each of the mixtures were admixed for 5 to 15 minutes with 200ml of pure water or 200ml of diluted aqueous solution of hydrochloric acid of pH8, and the concentration of mercury in the water was measured.

The results are listed in Table 4.

TABLE 4

fixing agent			mud (parts)	water (parts)	mixing time (min.)	Pure water (p) or HCl aqueous solution (HCl)	Mercury concentration in water (ppm)					
							time					
							1 hour	1 week	1 month	3 months	6 months	1 year
1	0.5	100	0	10	P	P	0.003	0.003	0.002	** < 0.001	< 0.001	< 0.001
						HCl	0.006	0.004	0.004	0.002	0.001	0.001
2	0.5	100	0	15	P	P	0.005	0.003	0.003	0.001	< 0.001	< 0.001
						HCl	0.007	0.005	0.003	0.002	0.001	0.001
3	0.2	100	5	10	P	P	0.005	0.003	0.003	0.002	0.001	< 0.001
						HCl	0.008	0.006	0.005	0.002	0.001	0.001
5	0.1	100	0	15	P	P	0.005	0.005	0.003	0.003	0.002	0.001
						HCl	0.007	0.005	0.004	0.004	0.002	0.002
6	1.0	100	0	5	P	P	0.005	0.003	0.002	0.001	0.001	< 0.001
						HCl	0.006	0.004	0.003	0.001	0.001	< 0.001
7	0.3	100	0	10	P	P	0.005	0.004	0.004	0.003	0.001	< 0.001
						HCl	0.008	0.005	0.004	0.004	0.002	0.002
8	0.5	100	0	15	P	P	0.007	0.006	0.006	0.003	0.002	0.001
						HCl	0.009	0.006	0.007	0.004	0.003	0.003

TABLE 4 (Continued)

fixing agent		mud (quarts)	water (pints)	mixing time (min.)	Pure water (p) or HCl aqueous solution (HCl)	Mercury concentration in water (ppm)					
						time					
Nix in Test 1	(pints) %					1 hour	1 week	1 month	3 months	6 months	1 year
12	0.3	100	0	10	P	0.005	0.003	0.003	0.002	0.001	0.001
					HCl	0.006	0.005	0.003	0.003	0.002	0.001
13	0.1	100	0	15	P	0.006	0.005	0.003	0.003	0.003	0.002
					HCl	0.008	0.006	0.005	0.005	0.004	0.003
14	0.2	100	0	10	P	0.005	0.005	0.003	0.002	0.001	0.001
					HCl	0.006	0.005	0.005	0.004	0.003	0.002
17	0.5	100	0	10	P	0.005	0.005	0.003	0.003	0.001	0.001
					HCl	0.006	0.005	0.004	0.004	0.003	0.002
20	0.3	100	0	10	P	0.005	0.004	0.004	0.003	0.003	0.001
					HCl	0.007	0.005	0.005	0.004	0.004	0.003
none(control)		100	0	0	P	0.030	0.05	0.040	0.055	0.067	0.072
					HCl	0.12	0.19	0.22	0.44	0.61	0.75

* converted into nett content of active ingredient

** .0.001 means less than 0.001

Example 29.
100 parts of copper sludge byproduct of a copper electro-plating factory were adjusted to pH7, and 1.0 to 0.5 part of fixing agent (as net content of effective compound) was added to the sludge and mixed for 10 minutes. Then the sludge was tested by the same method as for Example 28, and the concentration of copper in extracting water was measured.

The results are listed in Table 5, in which the fixing agents are identified by the numbers given in Table 1.

TABLE 5

fixing agent		copper sludge (parts)	mixing time (min.)	concentration of copper (ppm)			
				time			
number in Table 1	(parts)			1 hour	1 week	1 month	3 months
5	1.0	100	10	not detected*	not detected	not detected	not detected
3	0.5	100	15	"	"	"	"
13	0.5	100	10	"	"	"	"
17	1.0	100	10	"	"	"	"
20	1.0	100	15	"	"	"	"
0 (control)	—	100	0	12	19	17	14

* less than 0.1 ppm

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Example 30.
100 parts of cadmium sludge (containing 13 ppm of cadmium and 73.5% water) by product of a factory using cadmium was adjusted to pH8 and 0.1 to 0.5 parts of fixing agent (as net content of effective compound) was added to the sludge and mixed for 10 minutes. Then the sludge was tested by the same method as for Example 28 and the concentration of cadmium in extracting water was measured.

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The results are listed in Table 6.

TABLE 6

fixing agent number in Table 1	cadmium sludge (parts)	mixing time (min.)	test water	concentration of cadmium (ppm)			
				time			
	(parts)			1 hours	1 week	1 month	3 months
1	0.1	10	water	0.01	0.01	0.01	0.01
			sea water	"	"	"	"
3	0.1	10	water	"	"	"	"
			sea water	"	"	"	"
4	0.2	10	water	"	"	"	"
			sea water	"	"	"	"
8	0.5	15	water	"	"	"	"
			sea water	"	"	"	"
14	0.1	10	water	"	"	"	"
			sea water	"	"	"	"
16	0.3	10	water	"	"	"	"
			sea water	"	"	"	"
17	0.5	15	water	"	"	"	"
			sea water	"	"	"	"
20	0.5	10	water	"	"	"	"
			sea water	"	"	"	"

TABLE 6 (Continued)

fixing agent		cadmium sludge (parts)	mixing time (min.)	test water	concentration of cadmium (ppm)			
					1 hours	1 week	1 month	3 months
number in Table 1	(parts)			water	0.6	0.5	0.4	0.5
0	-	100	0	sea water	0.8	1.1	1.0	0.8

* -0.01 means less than 0.01

270 parts of soil (containing 20.3 ppm of cadmium and 63% of water) from a peaty field and 1.0 to 0.3 parts of fixing agent were mixed together.

After 14 days, 14 days, 1 month, 3 months and 6 months, 10 gers of the soil were treated to the same water content with 5% and 10% of the fixing agent mixed with 50 ml of aqueous solution of citric acid (pH 4.3). The mixture was shaken for 1 hour and the concentration of extracted cadmium in the aqueous solution was measured.

The results and fixing agents are listed in Table 7, the fixing agents being identified by the numbers given in Table 1.

TABLE 7

fixing agent		concentration of cadmium (ppm)				
number in Table 1	(parts)	time				
		3 days	14 days	1 month	3 months	6 months
5	0.5	0.31	0.28	0.27	0.27	0.25
6	0.3	0.56	0.53	0.52	0.51	0.49
8	0.5	0.49	0.48	0.46	0.46	0.45
7	0.3	0.63	0.61	0.59	0.57	0.57
3	0.5	0.23	0.20	0.18	0.19	0.16
1	0.5	0.35	0.31	0.30	0.30	0.28
10	0.5	0.65	0.63	0.63	0.61	0.61
11	1.0	0.74	0.73	0.73	0.71	0.72
12	0.3	0.31	0.28	0.27	0.27	0.26
13	0.3	0.39	0.35	0.32	0.32	0.30
14	0.5	0.32	0.31	0.30	0.28	0.28
15	0.5	0.41	0.40	0.38	0.37	0.37
16	0.5	0.52	0.50	0.49	0.47	0.48
17	0.5	0.65	0.65	0.63	0.62	0.61
18	1.0	0.58	0.57	0.54	0.53	0.53
19	0.3	0.73	0.71	0.68	0.66	0.65
20	0.5	0.63	0.62	0.60	0.59	0.59
(control)	0	1.2	1.3	1.1	1.2	1.2

Example 32.

Soil (Ohiso-machi Nake-gun Kanagawa-ken Japan) was dried for 11 days at room temperature and for 5 hours at 110°C. 900 grs of the soil were placed in each of a number of pots each of 11.5cm inside diameter and 11cm height, and an aqueous solution of $\text{CdSO}_4 \cdot 4\text{H}_2\text{O}$ was added to the extent that the total cadmium content in the soil was 20ppm. Then 4 ml of fertilizer containing 120mg of KH_2PO_4 , 40mg of KCl and 320mg of $(\text{NH}_4)_2\text{SO}_4$ and 250ml of water were added to the soil in each pot. After 1 day, 0.003%, 0.03% or 0.3% of a fixing agent was admixed with the soil in each pot. After 4 days, 100 to 200ml of water were added, and 15 grains of rice seeds were planted in the soil in each pot.

The depths of water in each pot was kept at 2cm above the surface of the soil. Each pot was left for 50 days in a greenhouse under continuous lighting. After 50 days the rice plants were pulled out and washed. The concentration of cadmium in the roots, or stalks and leaves of the plants was measured.

The results and fixing agents used are listed in Table 8, the fixing agents being identified by the numbers given in Table 1.

TABLE 8

amount of agent	0.01 %				0.1 %				1.0 %			
	stalks & leaves		roots		stalks & leaves		roots		stalks & leaves		roots	
	Cd (ppm)	inhibition rate (%)	Cd (ppm)	inhibition rate (%)	Cd (ppm)	inhibition rate (%)	Cd (ppm)	inhibition rate (%)	Cd (ppm)	inhibition rate (%)	Cd (ppm)	inhibition rate (%)
fixing agent numbers in Table I												
No. 21	9.7	15	204	20	10.6	7	132	49	0.6	95	18	93
No. 22	9.8	14	151	41	6.2	46	108	58	1.4	88	10	96
No. 23	8.0	30	191	26	8.6	25	98	62	1.4	88	5	98
No. 24	11.5	0	198	23	6.9	39	149	58	1.1	90	10	96
No. 25	10.0	12	221	14	6.9	39	70	73	1.4	88	13	95
No. 8	9.4	18	170	34	7.9	31	97	62	1.4	88		
No. 15	10.8	5	205	20	4.8	42	184	28	2.1	82		90
(control) none	stalks and leaves: 11.4 ppm roots: 237 ppm											
(control) (cadmium was not added)	stalks and leaves: 0.5 " roots: 4.3 "											

note: No. 21, No. 22 and No. 25 made leaves deeper green.

WHAT WE CLAIM IS:—

1. A method of treating a slurry or solution containing heavy metal or heavy metallic compound to fix the metal or metallic compound, comprising the step of mixing with the solution or slurry 0.1 to 50.0% by weight of an aliphatic dithiocarbamate compound, wherein the aliphatic dithiocarbamate compound is a compound having an aliphatic chain, which may contain a nitrogen atom in place of a carbon atom, and at least two dithiocarbamic acid groups



or alkali metal, alkaline earth metal or ammonium hydroxide salts or esters thereof.

2. A method as claimed in claim 1, wherein the aliphatic dithiocarbamate compound is present in a cement composition in an amount of 0.001 to 10% by weight of the composition, and the composition is mixed in the slurry or solution in an amount of 20 to 80% by weight.

3. A method of treating soil containing heavy metal or metallic compound to prevent plants from absorbing the metal or metallic compound, comprising the step of mixing in the soil 0.001 to 10% by weight of an aliphatic dithiocarbamate compound, wherein the aliphatic dithiocarbamate compound is a compound having an aliphatic chain, which may contain a nitrogen atom in place of a carbon atom, and at least two dithiocarbamic acid groups



or alkali metal, alkaline earth metal or ammonium hydroxide salts or esters thereof.

4. A method as claimed in claim 3, wherein 0.01 to 2.0% by weight of the compound is mixed with the soil.

5. A method as claimed in any one of claims 1 to 4, wherein the aliphatic dithiocarbamate compound is a compound selected from ethylenedithiocarbamic acids, poly-(dithiocarboxyl)diethylenetetramines, poly(dithiocarboxyl)triethylene tetramines, poly-(dithiocarboxyl)tetraethylenepentamines and alkali metal or alkali earth metal salt of these amines

6. A method as claimed in any one of claims 1 to 4, wherein the aliphatic dithiocarbamate compound is selected from propylenedithiocarbamic acids, poly(dithiocarboxyl) dipropylene triamines, poly(dithiocarboxyl) tripropylenetetramines, poly(dithiocarboxyl)tetrapropylene pentamines and poly(dithiocarboxyl) penta-propylenhexamines.

7. A method as claimed in any one of claims 1 to 4, wherein the compound is prepared by reacting amines selected from ethylene diamine, diethylene triamine, triethylenetetramine, tetraethylenepentamine, pentaethylenhexamine, propylenediamine, dipropylene triamine, tripropylenetetramine, tetrapropylene pentamine and penta-propylenhexamine with carbon bisulfide, one gram molecule of amine to 2 to 6 gram molecules of carbon bisulfide being employed.

8. A construction cement having a heavy metal or heavy metallic compound fixing agent, the agent being present in an amount of 0.001 to 10% by weight and comprising a compound prepared by reacting an amine selected from ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, propylenediamine, dipropylene triamines tripropylene tetramine, tetrapropylene pentamine and pentapropylenhexamine with carbon bisulfide, one gram molecule of amine to 2 to 6 gram molecules of carbon bisulfide being employed.

9. A method as claimed in any one of claims 1 to 4, wherein the compound is prepared substantially as hereinbefore described with reference to any one of Examples 1 to 25.

10. A method as claimed in claim 1, substantially as hereinbefore described with reference to either Example 26 or Example 27.

11. A method as claimed in claim 1, substantially as hereinbefore described with reference to any one of Examples 28 to 30.

12. A method as claimed in either claim 3 or claim 5, substantially as hereinbefore described with reference to either Example 31 or Example 32.

DR WALTHER WOLFF & CO.,
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